

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 347 342 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
24.09.2003 Bulletin 2003/39

(51) Int Cl.7: **G03G 9/087**

(21) Application number: **03006072.7**

(22) Date of filing: **19.03.2003**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IT LI LU MC NL PT RO SE SI SK TR**  
Designated Extension States:  
**AL LT LV MK**

(30) Priority: **20.03.2002 JP 2002077856**

(71) Applicant: **Ricoh Company Ltd.**  
**Tokyo 143-8555 (JP)**

(72) Inventors:  
• **Masuda, Minoru**  
**Ohta-ku, Tokyo 143-8555 (JP)**  
• **Asahina, Yasuo**  
**Ohta-ku, Tokyo 143-8555 (JP)**

- **Mochizuki, Satoshi**  
**Ohta-ku, Tokyo 143-8555 (JP)**
- **Umemura, Kazuhiko**  
**Ohta-ku, Tokyo 143-8555 (JP)**
- **Iwamoto, Yasuaki**  
**Ohta-ku, Tokyo 143-8555 (JP)**
- **Sugiura, Hideki**  
**Ohta-ku, Tokyo 143-8555 (JP)**
- **Tamura, Tomomi**  
**Numazu-shi, Shizuoka (JP)**

(74) Representative: **Barz, Peter**  
**Patentanwalt**  
**Kaiserplatz 2**  
**80803 München (DE)**

(54) **Toner for electrophotography**

(57) The present invention aims to provide a safer toner having lower content of residual bisphenol A, which has been suspected of an endocrine disrupting chemical.

A toner for electrophotography which contains a coloring agent, and a binder resin, in which the binder resin is a polyol resin which is prepared by reacting a) an epoxy resin, b) a compound having one or more active hydrogen atoms which react with an epoxy group in

molecules of the compound having one or more active hydrogen atoms, and c) a compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms, a weight concentration of unreacted bisphenol A in the toner is 1000 µg/g or less, and the toner has an epoxy equivalent of 20000 or more.

**EP 1 347 342 A1**

## Description

## BACKGROUND OF THE INVENTION

## Field of the Invention

[0001] The present invention relates to a toner for electrophotography.

## Description of the Related Art

[0002] With an electrophotographic method, a latent electrostatic image is formed on a photoconductor by a conventional method, and developed with a dry toner. Thereafter, the resulting toner image is transferred onto a sheet of copy paper, and is fixed onto the sheet by thermal fixing (generally, using a heat roller) so as to obtain a copy image. As generally known, the dry toner for this method contains a binder resin and a coloring agent as the main components. If required, the dry toner may further contain additives, such as a charge control agent and an offset-preventing agent.

[0003] Here, examples of the binder resins are polystyrenes, styrene-acrylic copolymers, polyester resins, epoxy resins, and the like, in terms of the properties required for the toner, for instance, transparency, insulating properties, water-resistance, flowability (as a powder), mechanical strength, glossiness, thermoplasticity, grindability, and the like. Of these, styrene resins are widely used because of the excellent grindability, water-resistance, and flowability.

[0004] However, when a sheet of paper bearing a copy image formed by a toner containing a styrene resin is held in a document folder made of a vinyl chloride resin sheet for storage, the side on which an image is formed is left in intimate contact with the resin sheet.

[0005] Accordingly, a plasticizer contained in the resin sheet, which is formed of the vinyl chloride resin, is transferred to the fixed toner image, and plasticizes the fixed toner image. The plasticizer is then fused onto a side of the resin sheet. As a result, if the side on which an image is formed is separated from the resin sheet, unfavorably, the toner image is partially or entirely peeled from the image, and the resin sheet is also contaminated. Such a deficiency can also be observed for a polyester resin-containing toner.

[0006] As a countermeasure for preventing the transfer onto the vinyl chloride resin sheet, Japanese Patent Application Laid-Open (JP-A) No. 07-77832 discloses the use of a polyol resin synthesized by using an epoxy resin as a raw material.

[0007] Such a polyol resin uses an epoxy resin and bisphenol A as raw materials. The epoxy groups in the epoxy resin and the active hydrogen moiety of bisphenol A are allowed to react with each other to perform synthesis. Epoxy groups in the epoxy resin are chemically very active, and, biochemically, considered to have a toxicity such as skin irritation. For this reason, for the synthesis of a polyol resin, the number of moles of the active hydrogen atoms is set to be larger than the number of moles of the epoxy groups. Accordingly, all of the epoxy groups are allowed to react, so that no epoxy group is left, resulting in a polyol resin.

[0008] However, some active hydrogen atoms remain, and hence bisphenol A used as a raw material also partially remains unreacted in the resulting polyol resin.

[0009] In recent years, bisphenol A has been suspected of being an endocrine disrupting chemical, and hence it is considered to possibly cause a problem in terms of the safety of the toner.

## SUMMARY OF THE INVENTION

[0010] It is an object of the present invention to provide a safer toner by controlling the amount of the residual bisphenol A, which is suspected of being an endocrine disrupting chemical, in the toner to 1000  $\mu\text{g/g}$  or less in weight concentration.

[0011] Further, it is another object of the present invention to provide a toner for electrophotography which, even if the fixed image side of the copy image-bearing paper sheet is brought in intimate contact with a vinyl chloride resin sheet, the toner image is not transferred to the vinyl chloride resin sheet.

[0012] Still further, it is a still another object of the present invention to provide a toner for electrophotography whereby the resulting image is excellent in color reproducibility and has stable glossiness not causing non-uniformity.

[0013] The present invention provides, in a first aspect, a toner for electrophotography which is characterized by containing a coloring agent and a binder resin. In the toner of the present invention, the binder resin is a polyol resin which is prepared by reacting a) an epoxy resin, b) a compound having one or more active hydrogen atoms which react with an epoxy group in molecules of the compound having one or more active hydrogen atoms, and c) a compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms, in which a weight concentration of non-reacted bisphenol A in the toner is 1000  $\mu\text{g/g}$  or less, and the toner has an epoxy equivalent of 20000 or more.

[0014] The present invention also provides, in a second aspect, an image-forming process in which a latent electrostatic image on a latent electrostatic image support is developed by the toner of the present invention.

[0015] The present invention further provides, in a third aspect, an image-forming apparatus which includes an image developer where the toner of the present invention is utilized as a developer.

[0016] The present invention still further provides, in a fourth aspect, an image-forming process cartridge. The image-forming process cartridge of the present invention includes an image developer configured to supply a developer onto a latent electrostatic image so as to visualize and develop the latent electrostatic image. The image-forming process cartridge of the present invention is formed in one-piece construction, and is attachable to and detachable from an image-forming apparatus. The developer in the image-forming process cartridge of the present invention contains the toner of the present invention.

#### BRIEF DESCRIPTION OF THE DRAWING

[0017] A single FIGURE is a diagram showing one example of the image-forming process cartridge of the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] The toner for electrophotography of the present invention contains a coloring agent and a binder resin, and if required, other materials may be added thereto.

(Binder resin)

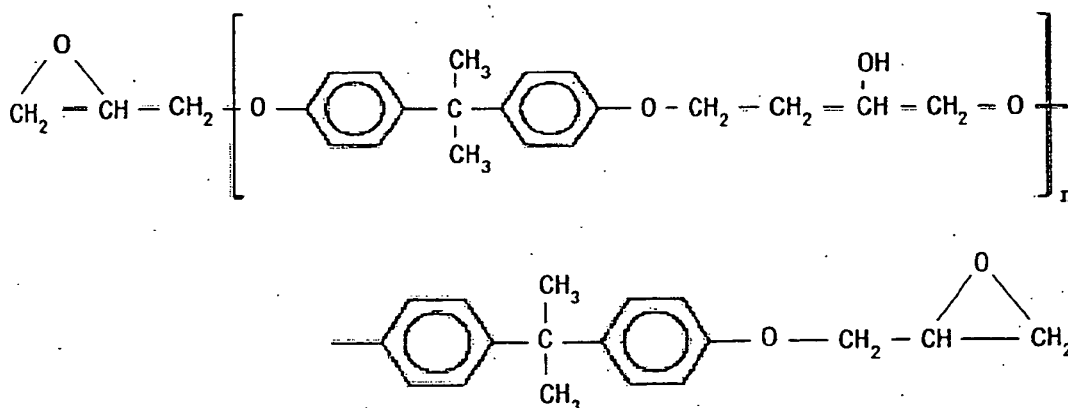
[0019] As the binder resin, a polyol resin is preferably used.

-Polyol resin-

[0020] The polyol resin to be used in the present invention is synthesized in the following manner. A compound having active hydrogen atoms which react with epoxy groups is used as a raw material. This compound and an epoxy resin are allowed to react with each other so that the resulting reaction product has a linear chain or network molecular structure. Namely, in order that the resulting polyol resin may have a linear chain or network molecular structure, a compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms is used as a raw material to enlarge the molecule. Further, for achieving a proper molecular weight in synthesizing the polyol resin, a compound having one or more active hydrogen atoms which react with an epoxy group in molecules of the compound having one or more active hydrogen atoms is used to cap the end of the resin molecule, thereby preventing the resin molecule from increasing in size.

-Epoxy resin-

[0021] Any epoxy resin may be used in the present invention so long as it has two or more epoxy bonds. In general, the bisphenol A-type epoxy resins expressed by the following Formula (2) are typical ones. These are low priced and readily available also on a chemical industrial scale, and also chemically stable. In the present invention, such an epoxy resin obtained by bonding the bisphenol such as bisphenol A with epichlorohydrin is used in part, because it favorably results in a low cost.



Formula (2)

wherein "n" expresses 0 or more.

[0022] The epoxy resin to be used in the present invention is preferably obtained by bonding bisphenol such as bisphenol A with epichlorohydrin. In order to obtain stable image-fixing properties and glossiness, the epoxy resin includes at least two or more kinds of bisphenol A-type epoxy resin components having different number-average molecular weights. The number-average molecular weight of the low molecule weight is 360 to 2000, and the number-average molecular weight of the high molecule weight is 3000 to 10,000. Further, the content of the low molecule weight is 20 % by weight to 50 % by weight relative to the amount of the polyol resin, and the content of the high molecule weight is 5 % by weight to 40 % by weight, relative to the amount of the polyol resin.

[0023] When the low molecule weight is present in too large amounts, or has a molecular weight of still lower than 360, too much glossiness may occur, and further the storageability may deteriorate. Moreover, when the high molecule weight is present in too large amounts, or has a molecular weight of still higher than 10,000, the glossiness of the resulting image may be insufficient, and further the image-fixing properties may deteriorate.

- Compound having one or more active hydrogen atoms which react with an epoxy group in molecules of the compound having one or more active hydrogen atoms -

[0024] Examples of the compound having one active hydrogen atom which reacts with an epoxy group in the molecule to be used in the present invention may include monovalent phenols, secondary amines, carboxylic acid, and the like. Examples of the monovalent phenols include phenol, cresol, isopropylphenol, aminophenol, nonylphenol, dodecylphenol, xylenol, p-cumylphenol, and the like. Examples of the secondary amines include diethylamine, dipropylamine, dibutylamine, N-methyl(ethyl)piperazine, piperazine, and the like. Examples of the carboxylic acids include propionic acid, caproic acid, benzoic acid, stearic acid, and the like.

- Compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms -

[0025] Examples of the compound having two or more active hydrogen atoms which reacts with epoxy groups in the molecule to be used in the present invention include dihydric phenols, multivalent phenols, multivalent carboxylic acids, and the like.

[0026] Examples of the dihydric phenols may include bisphenols such as bisphenol A, bisphenol F, or the like. Examples of the multivalent phenols may include ortho-cresol novolaks, phenol novolaks, tris(4-hydroxyphenyl)methane, 1-[α-methyl-α-(4-hydroxyphenyl)ethyl]benzene, and the like.

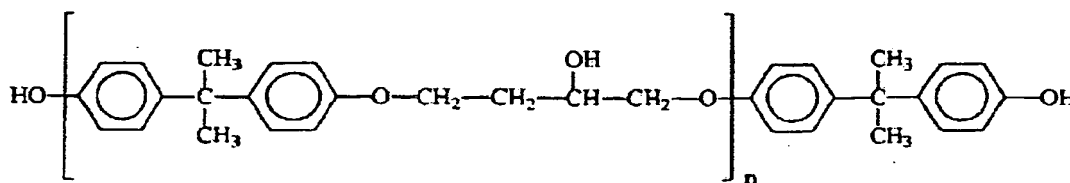
[0027] Examples of the multivalent carboxylic acids include malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid, terephthalic acid, trimellitic acid, trimellitic anhydride, and the like. The use of bisphenol A is excellent in terms of cost, and enables improving the chemical resistance of the toner resin. Furthermore, the use of bisphenol A also perfectly prevents toners from being transferred onto a vinyl chloride resin sheet.

(Weight concentration of unreacted bisphenol A)

[0028] In the present invention, the amount of residual bisphenol A in the toner, which has been suspected of an endocrine disrupting chemical in recent years, is set to be 1000 µg/g or less from the viewpoint of the safety of the toner. Hereinafter, a description will be given to a process for reducing the amount of residual bisphenol A.

[0029] If some other compound than the bisphenol A is used as the compound having two or more active hydrogen atoms which react with epoxy groups, no bisphenol A will remain. However, as a polyol resin, the one containing bisphenol A as the skeleton, is preferably used if possible, when considering the chemical resistance.

[0030] Thus, as a process for forming a polyol resin comprising bisphenol A as the skeleton, and free of residual bisphenol A, the following process is preferably used. Namely, as the compound having two or more active hydrogen atoms which react with epoxy groups, the compound expressed by the following Formula (3) is used:



Formula (3)

wherein "n" expresses an integer of 1 or more.

[0031] It is possible to obtain the above-described compound as the one free of residual bisphenol A, by allowing epichlorohydrin and bisphenol A to react with each other in an appropriate ratio. Conventionally, this process for reacting epichlorohydrin and bisphenol A has not been employed, because the viscosity of the resin increases with this method, the amount of a solvent becomes larger than in a case that the bisphenol A is used alone. Accordingly, the cost increases. However, the use of the process is most preferred, considering the safety of the toner and the acquisition of chemical resistance.

[0032] Further, it is also possible to set the amount of residual bisphenol A at 1000 µg/g or less, by using bisphenol A. This can be achieved by making the number of epoxy groups in the epoxy resin equal to the number of active hydrogen atoms which react with epoxy groups with high accuracy.

[0033] If the number of epoxy groups is set to be larger than the number of active hydrogen atoms which react with epoxy groups, bisphenol A having active hydrogen atoms will not remain alone, but epoxy groups will remain in the resin. The epoxy groups are chemically active, and considered to have a toxicity such as skin irritation, or the like. For this reason, in the related art, the number of active hydrogen atoms which react with epoxy groups has been set to be larger than the number of epoxy groups, so that no epoxy groups remain. However, with this method, the compounds such as bisphenol A having active hydrogen atoms will remain in a slight amount.

[0034] In the present invention, by making the number of epoxy groups in the epoxy resin equal to the number of active hydrogen atoms which react with epoxy groups with high accuracy, it is possible to eliminate epoxy groups in the polyol resin, and to control the amount of residual bisphenol A to 1000 µg/g or less. In addition, it should also be noted that the raw materials are weighed with high accuracy, and that sufficient stirring is performed and sufficient time is taken for the reaction so as to leave no reaction residue.

[0035] Further, it is necessary to take into consideration the case where the number of epoxy groups becomes slightly larger than the number of active hydrogen atoms due to a variation in number of raw material epoxy groups, the purity of the raw material, weighing error, or the like. Specifically, by applying a sufficient reaction time and a sufficient temperature for the reaction, the alcoholic OH groups formed from the reaction of the epoxy groups and active hydrogen atoms, react with epoxy groups. For this reason, by applying a sufficient reaction time and temperature thereto, no epoxy groups will remain in the polyol resin.

(Method for determining the weight concentration of unreacted bisphenol A)

[0036] Hereinafter, a method for determining the concentration of unreacted bisphenol A which solely remains in a toner will be described. The weight concentration of the polar solvent soluble component of the present invention can be determined by, for example, the high performance liquid chromatography (HPLC) as shown below. There is also another method for determining the concentration by a gas chromatography. However, HPLC is preferred in terms of

accuracy.

**[0037]** A sample is dissolved in a toner-soluble or resin-soluble solvent (for example, tetrahydrofuran (THF), toluene, methylethylketone, dichloromethane, chloroform, or the like). Thereafter, to the resulting solution, a polar solvent such as methanol, or the like (for example, methanol, ethanol, n-propanol, acetonitrile, water, or a mixed solution thereof, or the like), is added, thereby forming a precipitate. Thus, an insoluble portion of the polar solvent is removed, and a soluble portion of the polar solvent is extracted. The extracted component is separated and subjected to the qualitative analysis by HPLC, followed by the quantitative analysis by using a standard sample.

**[0038]** Although detailed examples are shown below, any of the techniques are not limited to the following apparatus and conditions, so long as it is capable of analyzing the polar solvent soluble matter with high accuracy.

- 1) Method: high performance liquid chromatography (HPLC)
- 2) Apparatus: Alliance 2690, UV 2487 detector, manufactured by Waters Corporation
- 3) Conditions: column Develosil ODS-Hg-3 (manufactured by Nomura Chemical Co., Ltd.)

$\phi$  4.6mm  $\times$  150 mm  
 Moving phase: water / acetonitrile = 65/35  
 Flow rate 1.0 ml/min  
 Detection 228 nm  
 Injection amount 15  $\mu$ l

#### 4) Procedure for preparing a sample

1. One gram of a sample is accurately weighed, and is added into a 100ml Erlenmeyer flask;
2. 30ml of THF is added to the flask, and is dissolved therein;
3. Upon completing dissolving, 50 ml of methanol is added thereto, so as to form a precipitate;
4. After filtration with a 5A filter paper, the solvent is removed;
5. A constant volume is maintained with 5 ml of acetonitrile and 5 ml of distilled water;
6. The solution is filtrated through a filter, resulting in a HPLC sample; and
7. A standard sample is also prepared in the same manner.

**[0039]** The polyol resin to be used in the present invention employs an epoxy resin as a raw material. However, the polyol resin has no epoxy group because the epoxy group is chemically very active, and biochemically considered to have a toxicity such as skin irritation. Namely, the polyol resin of the present invention refers to a polyol resin which has an epoxy skeleton, but has no terminal epoxy substantially.

(Epoxy equivalent)

**[0040]** The epoxy equivalent is used for expressing the number of epoxy groups. The term, "epoxy equivalent," refers to the equivalent weight per epoxy group (g/equiv.). The value obtained by dividing the average molecular weight by the number of epoxy groups per molecule. The epoxy equivalent is determined in accordance with an indicator titration method defined in paragraph 4.2 of JIS K 7236. However, the epoxy equivalent has an identification limit of about 20,000. Thus, if it is 20,000 or more, it is considered that there are almost no epoxy groups.

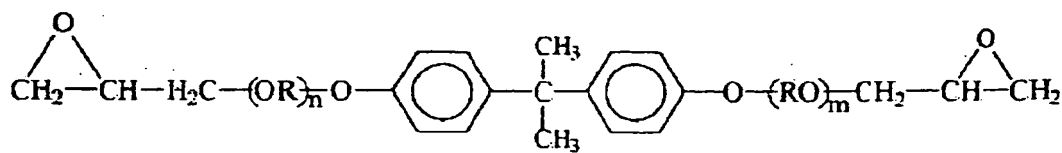
(Alkylene oxide adduct)

**[0041]** Using materials in which alkylene oxide is added to the polyol resin, preferably to bisphenols such as bisphenol A, gives a suitable flexibility to resins for the toner of the present invention. Accordingly, the toner of the present invention shows excellent image-fixing properties, and prevents curling on a fixed image.

**[0042]** In the present invention, methods for introducing the material obtained by adding an alkylene oxide to bisphenol include the following two methods.

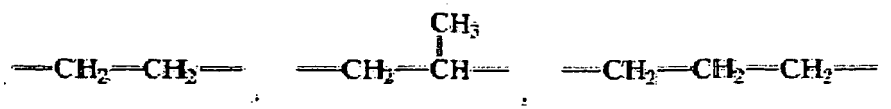
**[0043]** The first method is a method using a product of epoxidation reactive between the bisphenol-alkylene oxide adduct and epichlorohydrin. The reaction product is used as an epoxy resin for synthesizing a polyol resin.

**[0044]** Specific examples of the dihydric phenol-alkylene oxide adduct include reaction products of ethylene oxide, propylene oxide, butylene oxide, or mixture thereof, and bisphenol such as bisphenol A, bisphenol B, or the like. Further, the adduct thus obtained may also be glycidylated with epichlorohydrin or  $\beta$ -methylepichlorohydrin. In particular, a preferable example of the dihydric phenol-alkylene oxide adduct includes a diglycidyl ether of the bisphenol A-alkylene oxide adduct expressed by the following Formula (1).



Formula (1)

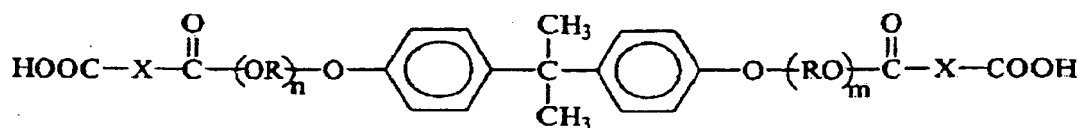
(where R is:



"n" and "m" each express the number of repeated units, each of "n" and "m" expresses 1 or more; and satisfies a relation of:  $n + m = 2$  to 8).

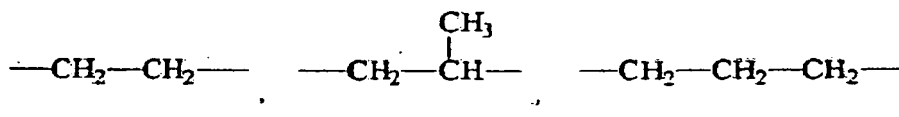
[0045] Further, the dihydric phenol-alkylene oxide adduct or a diglycidyl ether thereof is preferably contained in an amount of 10 to 40 % by weight relative to the amount of the polyol resin. If the content of the dihydric phenol-alkylene oxide adduct is low, the toner resin itself has no flexibility, and, unfavorably, a printed copy paper tends to curl increasingly, the toners are insufficiently fixed onto a copy paper, or other deficiencies occur. If "n + m" is equal to 9 or more, or the content is too high, the image transferred from the copy fixed image side to the vinyl chloride resin sheet may become more likely to occur, too much glossiness may occur, and further the storageability may deteriorate.

[0046] The second method is a method using a compound prepared by ester-bonding a polyvalent carboxylic acid to the dihydric phenol-alkylene oxide adduct such as bisphenol A as a compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms. In particular, the compound expressed by the following Formula (4) is preferred.



Formula (4)

(where R is:



"n" and "m" each express the number of repeated units, each of "n" and "m" is 1 or more; and satisfies a relation of:  $n + m = 2$  to 8)

[0047] Examples of the polyvalent carboxylic acids may include malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid, terephthalic acid, trimellitic acid, trimellitic anhydride, and the like.

[0048] Further, the compound prepared by allowing the dihydric phenol-alkylene oxide adduct and a polyvalent carboxylic acid to react is preferably contained in an amount of 10 % by weight to 40 % by weight relative to the amount

of the polyol resin. If the content thereof is low, the toner resin itself has no flexibility, a printed copy paper is more likely to curl, and, unfavorably, the toners are insufficiently fixed onto paper, or other deficiencies occur. If "n + m" is equal to 7 or more, or the content is too high, the image is transferred from a side on which the image is fixed, to the vinyl chloride resin sheet may become more likely to occur, too much glossiness may occur, and further the storageability may deteriorate.

[0049] The Tg of the resulting resin is preferably from 50°C to 70 °C, and more preferably from 55°C to 70 °C. If the Tg is low, agglomerate tends to occur in a toner bottle or a development unit. As a result, the agglomerate is also developed. The developed agglomerate remains on the photoconductor, and leaves one or more white spots on an image, when the toners are transferred. On the other hand, if the Tg is high, unfavorably, image glossiness tends to be insufficient.

(Coloring agent)

[0050] Any known dyes and pigments can be used as the coloring agents. Examples of the coloring agent include carbon black, nigrosine dyes, black oxide of iron, Naphthol Yellow S, Hansa Yellow (10G, 5G, G), cadmium yellow, yellow iron oxide, yellow ochre, chrome yellow, titan yellow, polyazo yellow, oil yellow, Hansa Yellow (GR, A, RN, R), Pigment Yellow L, benzidine yellow (G, GR), permanent yellow (NCG), vulcan fast yellow (5G, R), tartrazine lake, quinoline yellow lake, anthracycline yellow BGL, isoindolinone yellow, red oxide, red lead oxide, red lead, cadmium red, cadmium mercury red, antimony red, permanent red 4R, para red, Fire Red, para-chloro-ortho-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRL, F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, bordeaux 5B, toluidine maroon, permanent bordeaux F2K, helio bordeaux BL, bordeaux 10B, BON maroon light, BON maroon medium, eosine lake, rhodamine lake B, rhodamine lake Y, alizarine lake, thioindigo red B, thioindigo maroon, oil red, quinacridone red, pyrazolone red, polyazo red, chrome vermilion, benzidine orange, perylene orange, oil orange, cobalt blue, cerulean blue, alkali blue lake, peacock blue lake, victoria blue lake, metal-free phthalocyanine blue, phthalocyanine blue, fast sky blue, indanthrene blue (RS, BC), indigo, ultramarine, Prussian blue, anthraquinone blue, fast violet B, methyl violet lake, cobalt violet, manganese violet, dioxan violet, anthraquinone violet, chrome green, zinc green, chrome oxide, Persian, emerald green, pigment green B, naphthol green B, green gold, acid green lake, malachite green lake, phthalocyanine green, anthraquinone green, titanium oxide, zinc white, lithopone, and mixtures thereof, and the like.

[0051] In general, the coloring agent is preferably used in an amount of 0.1 part by weight to 50 parts by weight relative to 100 parts by weight of the binder resin.

(Other materials)

[0052] Then, a description will be given to other materials to be used for the toner of the present invention.

[0053] For the toner of the present invention, a so-called release agent for imparting the releasability to the toner may also be used. The softening point of the release agent to be used is preferably 70°C to 100 °C. The softening point of lower than 70 °C results in deficient storage stability. On the other hand, if the softening point is higher than 100 °C, not only the image-fixing properties tend to deteriorate, but also the resulting color image tends to be poor in quality because of its lower glossiness or the like.

[0054] Specific examples of the release agent may include synthesized waxes such as low-molecular weight polyethylene, low-molecular weight polypropylene, copolymers thereof, or the like; vegetable waxes such as candelilla wax, carnauba wax, rice wax, Japan tallow, jojoba wax, or the like; animal waxes such as bees wax, lanolin, spermaceti, or the like; mineral waxes such as montan wax, ozocerite, or the like; and grease waxes such as hardened castor oil, hydroxystearic acid, aliphatic acid amide, phenol aliphatic acid ester, and the like. From the viewpoint of chemical structures of the waxes, hydrocarbon waxes, ester waxes, amide waxes, and the like are known. However, in the present invention, ester waxes are preferable from the viewpoint of evaluating the storageability, image quality, the range of the fixing temperature, and the like.

[0055] The amount of the release agent is preferably 1 part by weight to 6 parts by weight relative to the total amount of the toner.

[0056] If the amount is larger than 6 parts by weight, the toner shows deficient storage stability, rough surface of an image, and lower glossiness. Further, even if the amount is less than 1 part by weight, the surface of an image tends to be rough, and the resulting color image tends to be poor in quality because of the lower glossiness or the like.

[0057] The toner of the present invention may contain a charge control agent, if required. Any known charge control agents can be used in the present invention. Examples of the charge control agent include a nigrosine dye, a triphenylmethane dye, a chromium-containing metal complex dye, a molybdenic acid chelate pigment, a rhodamine dye, an alkoxyamine, a quaternary ammonium salt (including a fluorine-modified quaternary ammonium salt), alkylamide, a



simplex or a compound of phosphorus, a simplex or a compound of tungsten, a fluorine-containing activator, a metallic salt of salicylic acid, a metallic salt of a salicylic acid derivative, and the like.

[0058] In addition, the toner of the present invention may further contain other additives, for example; silica fine particles, aliphatic metallic salts (such as zinc stearate, aluminum stearate, or the like), metallic oxides (such as titanium oxide, aluminum oxide, tin oxide, antimony oxide, or the like), fluoropolymers, and the like. In particular, hydrophobized silica, titania, and alumina fine particles are preferred.

[0059] Examples of the silica fine particles may include HDK H 2000, HDK H 2000/4, HDK H 2050EP, and HDK H 1303VP (all of which are manufactured by Clariant Ltd.), and R972, R974, RX200, RY200, R202, R805, and R812 (all of which are manufactured by Nippon Aerosil K.K.), and the like.

[0060] Further, examples of the titania fine particles may include P-25 (manufactured by Nippon Aerosil K.K.), STT-30, and STT-65C-S (all of which are manufactured by Titan Kogyo K.K.), TAF-140 (manufactured by Fuji Titanium Industry Co., Ltd.), and MT-150W, MT-500B, MT-600B (all of which are manufactured by Tayca Corp.), and the like.

[0061] In particular, as the hydrophobically treated titanium oxide fine particles, there can be used the anatase type or rutile type crystalline ones, or amorphous ones. Examples thereof may include T-805 (manufactured by Nippon Aerosil K. K.), and as the rutile type, MT-100S, MT-100T, MT150A, MT150AFM, and MT-150AI (all of which are manufactured by Tayca Corp.), STT-30A, STT-65S-S (all of which are manufactured by Titan Kogyo K.K.), TAF-500T and TAF-1500T (all of which are manufactured by Fuji Titanium Industry Co., Ltd.), MT-100S and MT-100T (all of which are manufactured by Tayca Corp.), IT-S (manufactured by Ishihara Sangyo Kaisha, Ltd.), and the like.

[0062] The hydrophobically treated silica fine particles, titania fine particles, or alumina fine particles can be obtained by treating hydrophilic fine particles with a silane coupling agent such as methyl trimethoxy silane, methyl triethoxy silane, octyl trimethoxy silane, or the like. Further, as additives, an aliphatic acid metal salt (such as zinc stearate or aluminum stearate), a metal oxide (such as alumina, tin oxide, or antimony oxide), and fluoropolymers, and the like may also be contained together.

[0063] The toner made of the materials as described above of the present invention may be used as a double-component developer in combination with a carrier shown below. Alternatively, the toner may be used alone as a single-component developer. The term, "developer," herein refers to any kinds of agent used for developing a latent electrostatic image.

[0064] When the toner is used as a double-component developer, as the carrier, the same materials as those employed in the related art such as iron powders, ferrite particles, glass beads, or the like can be employed. It is noted that these carrier may be coated with a resin. Known resins may also be used in this case. Examples of the resin may include acrylic resin, polyfluorocarbon, polyvinyl chloride, polyvinylidene chloride, phenolic resin, polyvinyl acetal, silicone resin, and the like.

[0065] In any case, as the mixing ratio of the toner to the carrier, in general, it is proper that the toner is mixed in an amount of 2.5 parts by weight to 8.0 parts by weight relative to 100 parts by weight of the carrier.

(Method for determining the softening point and the glass transition temperature)

[0066] The softening point and the Tg of the resin for use in the present invention are determined in the following manner.

[0067] First, the measurement is carried out using a full-automatic dropping point measurement apparatus "FP5/FP53" manufactured by Mettler Co., Ltd., as an apparatus for determining the softening point in accordance with the following procedure:

(1) A pulverized sample is placed in a fusing jar, and is allowed to stand for 20 minutes. The fused sample is then poured into a sample cup (with a dropping hole diameter of 6.35 mm) up to a brim of the sample cup, cooled to ordinary temperature, and then set in a cartridge;

(2) In the FP-5 control unit, a prescribed temperature elevation rate (1 °C/min) and measurement initiation temperature (set to be lower by 15 °C than the expected softening point, or less) are set;

(3) The cartridge is then set in a heating furnace of FP-53, and allowed to stand for 30 seconds. Thereafter, a start lever is pushed down, whereby the measurement is started (the subsequent measurement is automatically carried out);

(4) Upon completion of the measurement, the cartridge is detached; and

(5) The softening point (°C) is calculated in the following manner.

[0068] Value indicated in a result display panel A of FP-5 + Correction value

[0069] Note) The value obtained by adding the correction value to the result obtained corresponds to the result by Duran's mercury method.

[0070] Note) When the difference between the value displayed in the result display panel A and the measurement

initiation temperature (the value displayed in the panel B or C) is not 15 °C or more, the above test is once again carried out.

[0071] The measurement is carried out, using DSC-200 made by Seiko Instruments Inc., as an apparatus for determining the Tg in accordance with the following procedure:

- (1) A sample is pulverized, and 10±1 mg of the pulverized sample is weighed out in a sample container made of aluminum, and an aluminum lid is put thereon for crimping; and
- (2) The glass transition temperature (Tg) is determined in an atmosphere of nitrogen by the DSC method.

#### Analysis conditions

[0072] The sample is heated from room temperature up to 150 °C with a temperature increasing rate of 20 °C/min, and is then allowed to stand at 150 °C for 10 minutes. The sample is then cooled to 0 °C at a temperature decreasing rate of 50 °C/min, and is then allowed to stand for 10 minutes. In a stream of an atmosphere of nitrogen (20 cc/min), the sample is again heated up to 150 °C with a temperature increasing rate of 20 °C/min, and subjected to the DSC measurement. The Tg is measured by reading a peak rise-up temperature, using an analysis software "Tg Job."

[0073] The epoxy equivalent is measured in accordance with an indicator titration method defined in paragraph 4.2 of JIS K7236.

#### (Image-forming process)

[0074] An image-forming process of the present invention has no particular restriction, except that the toner for electrophotography of the present invention is used for developing a latent electrostatic image, and can be appropriately selected according to the intended purpose.

#### (Image-forming apparatus)

[0075] The image-forming apparatus of the present invention has no particular restriction, except that the image-forming apparatus accommodates an image developer in which the toner for electrophotography of the present invention is provided as a developing unit. The term, "image developer," herein refers to a developing device that enables developing a latent electrostatic image with a developer.

[0076] Aspects of the image developer, aspects of other configurations, and the like can be appropriately selected according to the intended purpose.

#### (Image-forming process cartridge)

[0077] Further, the image-forming process cartridge of the present invention is characterized by including a latent electrostatic image support; a charger configured to charge a surface of the latent electrostatic image support; a light-irradiator configured to irradiate a light to the latent electrostatic image; a cleaner configured to clean the surface of the latent electrostatic support; and an image developer configured to supply a developer onto a latent electrostatic image so as to develop the latent electrostatic image and to form a visible image. The image-forming process cartridge is formed in one-piece construction, and is attachable to and detachable from an image-forming apparatus. The image developer in the image-forming process cartridge of the present invention includes the developer which contains the toner for electrophotography including a color toner for forming an image according to the present invention.

[0078] When installed in an image-forming apparatus, the image-forming process cartridge provides sufficient offset-resistance even in a fixing step where no lubricant oil is coated on a fixing roller, or a very small amount of lubricant oil is coated on a fixing roller.

[0079] FIGURE shows an example of a structure of an image-forming process unit (process cartridge) (106), which includes all of a photoconductive drum (101) as the latent electrostatic image support, a charging roller (103) as the charger, a cleaning unit (105) as the cleaner, and a developing unit (102) as the image developer. The image-forming process cartridge is attachable to and detachable from a printer. The developing unit includes a developing sleeve (104).

[0080] Hereinafter, the present invention will be described by way of examples. It should be noted that "part(s)" expresses "part(s) by weight" in all of the cases.

[0081] Synthesis examples of a polyol resin which is used in the examples, will be firstly given.

#### (Synthesis Example 1)

[0082] 1000 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about

## EP 1 347 342 A1

1000), 50 g of terephthalic acid, 10 g of benzoic acid, and 300 g of xylene were added into a separable flask equipped with a propeller stirrer, a thermometer, a N<sub>2</sub> inlet, and a condenser tube. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin having a softening point of 108 °C and a Tg of 61 °C (which may be referred to as "resin 1," hereinafter).

[0083] The amount of residual bisphenol A was found to be 0 µg/g, and the epoxy equivalent was found to be 20,000 or more.

### (Synthesis Example 2)

[0084] 562 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 360), 104 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 2,700), 325 g of bisphenol A, 80 g of p-cumylphenol, and 300 g of xylene were added into a separable flask equipped with a propeller stirrer, a thermometer, a N<sub>2</sub> inlet, and a condenser tube. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 107 °C and a Tg of 58 °C (which may be referred to as "resin 2," hereinafter).

[0085] The amount of the residual bisphenol A was found to be 830 µg/g, and the epoxy equivalent was found to be 20,000 or more.

### (Synthesis Example 3)

[0086] Using the separable flask of Synthesis Example 1, 500 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 1000), 404 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 5000), 103 g of bisphenol A, 59 g of p-cumylphenol, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1000 g of a polyol resin with a softening point of 109 °C and a Tg of 58 °C (hereinafter, may be referred to as "resin 3").

[0087] The amount of residual bisphenol A was found to be 280 µg/g, and the epoxy equivalent was found to be 20,000 or more.

### (Synthesis Example 4)

[0088] Using the separable flask of Synthesis Example 1, 302 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 360), 100 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 3000), 336.0 g of a diglycidylated product of a bisphenol A type ethylene oxide adduct ["n+m" is about 5.9 in the aforementioned Formula (3)], 210 g of bisphenol A, 100 g of p-cumylphenol, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 109 °C and a Tg of 58 °C (hereinafter, may be referred to as "resin 4").

[0089] The amount of residual bisphenol A was found to be 950 µg/g, and the epoxy equivalent was found to be 20,000 or more.

### (Synthesis Example 5)

[0090] Using the separable flask of Synthesis Example 1, 310 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 680), 303 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 6,500), 300 g of a diglycidylated product of a bisphenol A-propylene oxide adduct ["n+m" is about 2.0 in the aforementioned Formula (3)], 50 g of stearic acid, 130 g of fumaric acid, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C

## EP 1 347 342 A1

for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 114 °C and a Tg of 60 °C (hereinafter, may be referred to as "resin 5").

[0091] The amount of residual bisphenol A was found to be 0 µg/g, and the epoxy equivalent was found to be 20,000 or more.

(Synthesis Example 6)

[0092] Using the separable flask of Synthesis Example 1, 398 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 680), 403 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 6,500), 199 g of a bivalent acid of a bisphenol A-propylene oxide adduct and phthalic anhydride condensation, 50 g of bisphenol A, 51 g of p-cumylphenol, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 112 °C and a Tg of 59 °C (hereinafter, may be referred to as "resin 6").

[0093] The amount of residual bisphenol A was found to be 620 µg/g, and the epoxy equivalent was found to be 20,000 or more.

(Synthesis Example 7)

[0094] Using the separable flask of Synthesis Example 1, 160 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 360), 170 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 3000), 170 g of a diglycidylated product of a bisphenol A-propylene oxide adduct ["n+m" is about 2.1 in the aforementioned Formula (3)], 380 g of a compound of bisphenol A expressed in the Formula (2) (number-average molecular weight: about 800), 200 g of p-cumylphenol, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 118 °C and a Tg of 62 °C (hereinafter, may be referred to as "resin 7").

[0095] The amount of residual bisphenol A was found to be 0 µg/g, and the epoxy equivalent was found to be 20,000 or more.

(Synthesis Example 8)

[0096] Using the separable flask of Synthesis Example 1, 1000 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 1000), 40 g of terephthalic acid, 10 g of benzoic acid, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 108 °C and a Tg of 61 °C (hereinafter, may be referred to as "resin 8").

[0097] The amount of residual bisphenol A was found to be 0 µg/g, and the epoxy equivalent was found to be 9380.

(Synthesis Example 9)

[0098] Using the separable flask of Synthesis Example 1, 390 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 680), 403 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 6,500), 199 g of a bivalent acid of a bisphenol A-propylene oxide adduct and phthalic anhydride condensation, 50 g of bisphenol A, 51 g of p-cumylphenol, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 112 °C and a Tg of 59 °C (hereinafter, may be referred to as "resin 9").

[0099] The amount of residual bisphenol A was found to be 8850 µg/g, and the epoxy equivalent was found to be 20,000 or more.

(Synthesis Example 10)

[0100] Using the separable flask of Synthesis Example 1, 435 g of a low-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 680), 403 g of a high-molecular weight bisphenol A-type epoxy resin (number-average molecular weight: about 6,500), 199 g of a bivalent acid of a bisphenol A-propylene oxide adduct and phthalic anhydride condensation, 50 g of bisphenol A, 51 g of p-cumylphenol, and 300 g of xylene were prepared in a separable flask. The resulting mixture was heated to 70 °C to 100 °C under a N<sub>2</sub> atmosphere, and 0.183 g of lithium chloride was added thereto. The resulting mixture was further heated to 160 °C, and xylene was distilled off under a reduced pressure. The mixture was polymerized at a reaction temperature of 180 °C for 6 to 9 hours, resulting in about 1 kg of a polyol resin with a softening point of 112 °C and a Tg of 59 °C (hereinafter, may be referred to as "resin 10").

[0101] The amount of residual bisphenol A was found to be 120 µg/g, and the epoxy equivalent was found to be 9800.

[Example 1]

[0102]

Manufacturing a toner	
Resin 1	100 parts
Cyan pigment (copper phthalocyanine)	4 parts
E-84 manufactured by Orient Chemical Industries Ltd. (a zinc complex used as a charge controlling agent)	2 parts

[0103] A mixture of the materials above was melt-kneaded by a hot roll mill. After cooling the mixture, the resulting mixture was roughly ground in a hammer mill, and then finely pulverized in an air-jet grinder. The resulting fine powder was classified to form a matrix toner having an average particle diameter of about 7 µm.

[0104] Thereafter, 0.8 part of a hydrophobic silica HDK2000H (manufactured by Clariant Japan K.K.) was mixed to 100 parts of the resulting matrix toner, so as to obtain a toner.

[Examples 2 to 7]

[0105] Each of the toners of Examples 2 to 7 was obtained in the same manner as in Example 1, except that the resin was altered to each of the resins of Synthetic Examples 2 to 7 in Example 1.

[Comparative Examples 1 to 3]

[0106] Each of the toners of Comparative Examples 1 to 3 was obtained with in the same manner as in Example 1, except that the resin was altered to each of the resins of Synthetic Examples 8 to 10 in Example 1.

[Comparative Example 4]

[0107] A toner of Comparative Example 4 was obtained with in the same manner as in Example 1, except that the resin of Example 1 was altered to a polyester resin. The polyester resin is a resin obtained from the condensation polymerization of a bisphenol A ethylene oxide adduct, a bisphenol A propylene oxide adduct, a terephthalic acid, and a fumaric acid in a molar ratio of 60 : 40 : 25 : 75. The polyester resin has a softening point of 107 °C and a Tg of 59°C.

(Result of Evaluation)

[0108] The amount of residual bisphenol A and the epoxy equivalent were measured with respect to each of the toners of Examples 1 to 7, and the toners of Comparative Examples 1 to 4.

[0109] Each of the toners of Examples 1 to 7, and the toners of Comparative Examples 1 to 4 was installed into a color copier Imagio Color 2800 manufactured by Ricoh Company Ltd., to produce image-bearing copy sheets. Each of the image-bearing copy sheets was brought in intimate contact with a vinyl chloride sheet, and then stored at 50 °C for 1 week to evaluate the adhesion of the toner to the vinyl chloride sheet.

[0110] Curl of the paper was also evaluated as to the toners of Examples 1 to 7 and the toners of Comparative Examples 1 to 4. The curl of the paper was measured based upon how the paper became curled up, when an image with 1mg/cm of the toners was transferred, and was then fixed onto paper.

[0111] The results of the evaluation are shown in Table 1.

[0112] The evaluation was ranked as follows:

⊙ : No problem at all

○ : No problem

Δ : Slightly troublesome but at an acceptable level

× : Problem occurred

Table 1

Evaluation results				
	Amount of residual bisphenol A [ $\mu\text{g/g}$ ]	Epoxy equivalent	Toner adhesion to vinyl chloride sheet	Curl of paper
Example 1	0	20000 or more	○	○
Example 2	780	20000 or more	⊙	○
Example 3	260	20000 or more	⊙	○
Example 4	890	20000 or more	⊙	⊙
Example 5	0	20000 or more	⊙	⊙
Example 6	580	20000 or more	⊙	⊙
Example 7	0	20000 or more	⊙	⊙
Comparative Example 1	0	9980	Δ	⊙
Comparative Example 2	8320	20000 or more	○	Δ
Comparative Example 3	110	10400	○	Δ
Comparative Example 4	0	20000 or more	×	×

[0113] As shown in Table 1, each of the toners of Examples of the present invention is characterized in that the amount of the residual bisphenol A is smaller, the epoxy equivalent is larger, and less toners adheres to the vinyl chloride sheet, compared with the toners of Comparative Examples.

[0114] The toner for electrophotography of the present invention enables obtaining a toner which contains less the residual bisphenol A and less residual epoxy groups. Hence the toner for electrophotography of the present invention enables obtaining a safer toner. Further, the toner for electrophotography of the present invention enables obtaining a toner which is less likely to adhere a vinyl chloride mat or the like, when used in a copied image.

## Claims

1. A toner for electrophotography comprising:

a coloring agent; and

a binder resin, wherein the binder resin is a polyol resin which is prepared by reacting:

a) an epoxy resin;

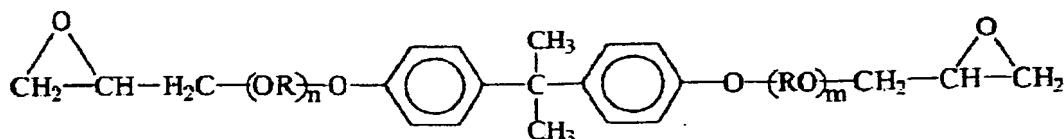
b) a compound having one or more active hydrogen atoms which react with an epoxy group in molecules of the compound having one or more active hydrogen atoms; and

c) a compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms,

wherein a weight concentration of non-reacted bisphenol A in the toner is 1000  $\mu\text{g/g}$  or less, and the toner has an

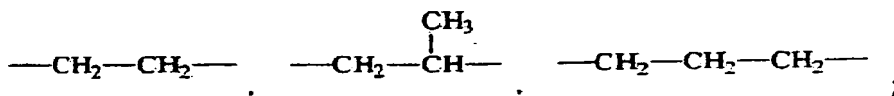
epoxy equivalent of 20000 or more.

2. A toner for electrophotography according to Claim 1, wherein the compound having two or more active hydrogen atoms which react with an epoxy group in molecules of the compound having two or more active hydrogen atoms contains bisphenol A.
3. A toner for electrophotography according to one of Claims 1 and 2, wherein the epoxy resin has two or more epoxy bonds.
4. A toner for electrophotography according to any one of Claims 1 to 3, wherein the epoxy resin contains two or more types of bisphenol A-type epoxy resins having different number average molecular weights.
5. A toner for electrophotography according to Claim 4, wherein the two or more types of bisphenol A-type epoxy resins having different number average molecular weights have:
  - 360 to 2000 of a number weight average molecular weight for low molecular weights of the bisphenol A-type epoxy resins; and
  - 3000 to 10000 of a number weight average molecular weight for high molecular weights of the bisphenol A-type epoxy resins.
6. A toner for electrophotography according to Claim 4, wherein the two or more types of bisphenol A-type epoxy resins having different number average molecular weights contain:
  - 20% by weight to 50% by weight of low molecular weights of the bisphenol A-type epoxy resins relative to the polyol resin; and
  - 5% by weight to 40% by weight of high molecular weights of the bisphenol A-type epoxy resins relative to the polyol resin.
7. A toner for electrophotography according to Claim 1, wherein the polyol resin contains a monomer unit of diglycidylether of a bisphenol A-alkyl oxide adduct expressed by the following Formula (1), as the epoxy resin:



Formula (1)

(where R is:



"n" and "m" each express the number of repeated units, each express an integer of 1 or more, and satisfy the relation of:  $n + m = 2$  to 8).

8. A toner for electrophotography according to Claim 1, wherein the toner contains 10% by weight to 40% by weight of the epoxy resin as a monomer unit relative to the amount of the polyol resin, and the epoxy resin is one of a dihydric phenol-alkylene oxide adduct, and a glycidyl ether of the dihydric phenol-alkylene oxide adduct.
9. A toner for electrophotography according to Claim 1, wherein the compound having two or more active hydrogen atoms which reacts with an epoxy group in molecules of the compound having two or more hydrogen atoms con-

tains a compound prepared by reacting a dihydric phenol-alkylene oxide adduct and a polyvalent carboxylic acid.

10. A toner for electrophotography according to Claim 9, wherein the polyvalent carboxylic acid is selected at least from malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid, terephthalic acid, trimellitic acid, and trimellitic acid anhydride.

11. A toner for electrophotography according to Claim 9, wherein the toner contains 10% by weight to 40% by weight of the compound having two or more active hydrogen atoms which react with an epoxy group, and the compound is a compound prepared by reacting a dihydric phenol-alkylene oxide and a polyvalent carboxylic acid.

12. A toner for electrophotography according to any one of Claims 1 to 11, wherein a glass transition temperature of the polyol resin is 50 °C to 75 °C.

13. A toner for electrophotography according to any one of Claims 1 to 12, further containing a release agent.

14. A toner for electrophotography according to Claim 13, wherein a softening point of the release agent is 70 °C to 100 °C.

15. A toner for electrophotography according to one of Claims 13 and 14, wherein a content of the release agent is 1 part by weight to 6 parts by weight, relative to the total amount of toners.

16. A toner for electrophotography according to any one of Claims 1 to 15, wherein a content of the coloring agent is 0.1 part by weight to 50 parts by weight relative to 100 parts by weight of the binder resin.

17. A toner for electrophotography according to any one of Claims 1 to 16, wherein the toner is utilized as a double-component developer.

18. An image-forming process **characterized in that** the image-forming apparatus includes the step of:

developing a latent electrostatic image,

wherein a toner for electrophotography according to any one of Claims 1 to 17 is utilized as a developer.

19. An image-forming apparatus **characterized in that** the image-forming apparatus contains:

an image developer,

wherein the image developer has a developer, and the developer contains a toner according to any one of Claims 1 to 17.

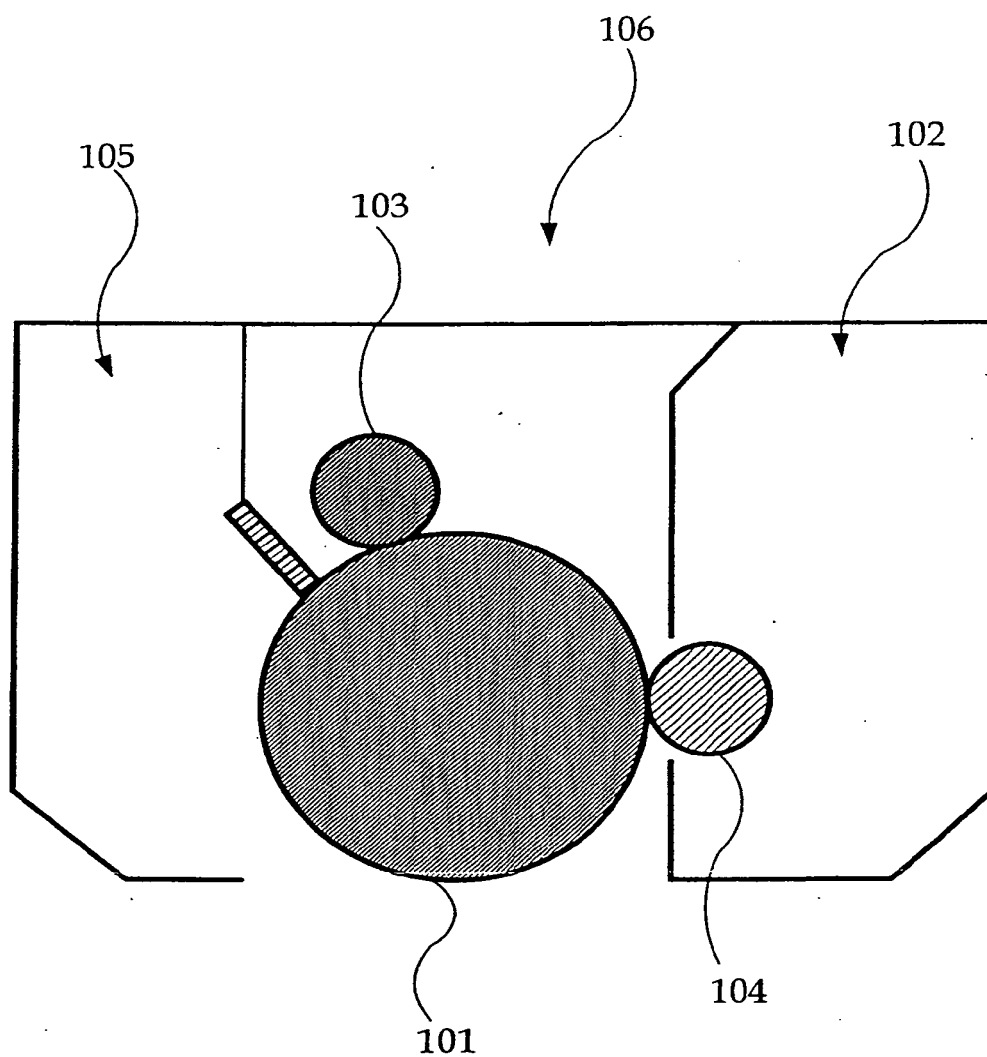
20. An image-forming process cartridge **characterized in that** the image-forming process cartridge contains:

an image developer configured to supply a developer to a latent electrostatic image so as to visualize and develop the latent electrostatic image,

wherein the image-forming process cartridge is formed in one-piece construction, and is attachable to and detachable from an image-forming apparatus, and the developer contains a toner according to any one of Claims 1 to 17.



FIGURE





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 03 00 6072

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 1 043 630 A (RICOH KK) 11 October 2000 (2000-10-11) * page 10, paragraph 101; claim 12 * * page 17; example 8 *	20	G03G9/087
A	US 5 998 073 A (KURAMOTO SHINICHI ET AL) 7 December 1999 (1999-12-07) * column 8; example 1 * * column 3, line 17 - column 4, line 55 *	1-20	
D,A	US 5 554 478 A (KURAMOTO SHINICHI ET AL) 10 September 1996 (1996-09-10) * column 8 - column 18; examples 1-22,24,25 *	1-20	
A	US 6 074 794 A (ASAHINA YASUO ET AL) 13 June 2000 (2000-06-13) * column 7; examples 1-5 *	1-20	
A	GB 1 550 555 A (OCE VAN DER GRINTEN NV) 15 August 1979 (1979-08-15) * page 2, left-hand column, line 26 - line 35 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03G
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		25 June 2003	Vogt, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 6072

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-06-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1043630 A	11-10-2000	EP 1043630 A2	11-10-2000
		JP 2000352841 A	19-12-2000
		US 6200719 B1	13-03-2001
US 5998073 A	07-12-1999	JP 10312087 A	24-11-1998
US 5554478 A	10-09-1996	JP 3313895 B2	12-08-2002
		JP 7077832 A	20-03-1995
		DE 19504299 A1	11-01-1996
US 6074794 A	13-06-2000	JP 11084719 A	30-03-1999
GB 1550555 A	15-08-1979	NL 7605372 A	22-11-1977
		AT 357866 B	11-08-1980
		AT 364777 A	15-12-1979
		AU 505953 B2	06-12-1979
		AU 2406977 A	12-10-1978
		BE 854860 A2	21-11-1977
		BE 879520 A5	15-02-1980
		CA 1115582 A1	05-01-1982
		CH 626731 A5	30-11-1981
		DE 2722974 A1	01-12-1977
		DK 218577 A ,B,	21-11-1977
		ES 458636 A1	01-02-1978
		FR 2352326 A1	16-12-1977
		IT 1082763 B	21-05-1985
		JP 1285134 C	09-10-1985
		JP 52143025 A	29-11-1977
		JP 60009264 B	08-03-1985
		NO 771488 A ,B	22-11-1977
		SE 435765 B	15-10-1984
		SE 7705868 A	21-11-1977

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82